

Chemical Analysis and Imaging Interfaces Focus Topic Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy, T. Mitch Wallis, S. Berweger, P. Kabos, National Institute of Standards and Technology** **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy, Sidney Cohen, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein, Weizmann Institute of Science, Israel; I. Rosenhek-Goldian, Weizmann Institute of Science, Israel; R. Weatherup, Oxford University, UK; B. Eren, Weizmann Institute of Science, Israel**

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO₂ reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod, Jiyoung Son, Pacific Northwest National Lab; J. Gao, PNNL; G. Sevigny, S. Tripathi, B. Matthews, Pacific Northwest National Lab; X. Yu, Oak Ridge National Laboratory**

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (³H) and lithium isotope (⁶Li, ⁷Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a

scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography, Si Chen, Argonne National Lab; Y. Luo, Argonne National Laboratory; T. Paunesku, Northwestern University; O. Antipova, Y. Liu, N. Zaluzeck, Z. Di, Argonne National Laboratory; G. Woloschak, Northwestern University** **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobe are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 In Situ Molecular Imaging of Green Solvents for CO₂ Capture, Xiao-Ying Yu, Oak Ridge National Laboratory, USA**

Switchable ionic liquids are emerging green solvents for carbon dioxide (CO₂) capture, cleaner separation, and efficient biomass production. However, the liquid structure and composition of SWILs are not fully understood. Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited. We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work. This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI). Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS. Two model systems are illustrated in this talk. The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO₂ loadings. The second has KOH with various CO₂ loadings. KOH acts as both acid and base in the latter. Our results show two coexisting liquid phases in these green solvents. This phenomenon was only hypothesized in previous theory prediction. We provide the first physical evidence of the complex liquid-liquid (l-l) interface using three-dimensional chemical mapping with submicrometer

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resolution. In addition, more complex stoichiometry is discovered due to CO₂ uptake. More importantly, we have provided the first chemical spatial visualization elucidating the evolving I – I interface. The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predictive material synthesis, CO₂ capture, and other versatile applications.

5:20pm CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy, A. Siebert, K. Goodman, **Monika Blum**, LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. CaCl₂, at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havalala O. T. Pye et al., *Atmos. Chem. Phys.*, 20, 4809–4888, 2020.

[2] Barbara J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.*, 2009, 11, 7760–7779.

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